

SLURRY COMPOSITIONS AND CMP METHODS USING THE SAME  
CROSS-REFERENCE TO RELATED APPLICATION

**[0001]** This application claims priority from Korean Patent Application No. 10-2003-0090551, which was filed on 12 December 2003 in the Korean Intellectual Property Office, the disclosure of which is incorporated herein in its entirety by reference.

BACKGROUND OF THE INVENTION

Field of the Invention

**[0002]** The present invention relates to slurry compositions and methods using such slurry compositions for the chemical mechanical polishing (CMP) of material layers deposited during the manufacture of semiconductor devices, more particularly to slurry compositions including one or more additives for adjusting the relative removal rates of different materials, and most particularly to slurry compositions including one or more additives for reducing the removal rate of polysilicon relative to other materials present on a semiconductor substrate.

Description of the Related Art

**[0003]** The increasing demand for high performance semiconductor devices and the corresponding demand for increased degrees of integration for modern semiconductor devices require the use of fine pitch multilayer interconnection structures. These multilayer interconnection structures are typically formed by processes that involve sequential insulator deposition, patterning, etching, conductor



deposition and planarization steps. The planarization steps are particularly important for providing a substantially planar surface for subsequent deposition and patterning processes that can consistently produce patterns having critical dimensions falling within narrow sizing ranges.

**[0004]** A variety of planarization methods have been utilized depending on the particular semiconductor fabrication process and the specific patterns and material layers being used at a particular step within the fabrication process. Planarization techniques have included forming a layer or a coating of an insulator, such as silicon dioxide, a conductor, such as copper, a resin, such as polyimide, a spin-on-glass (SOG), or a doped glass, such as borophosphosilicate glass (BPSG), followed by one or more processes such as etch-back, reflow, and/or CMP steps to obtain a more planar surface for subsequent processing.

**[0005]** In CMP processes, the semiconductor substrate is typically mounted on a rotating plate or other holder, and the surface of the substrate is then brought into contact with a polishing surface of a polishing pad. Portions of the material layers and/or patterns formed on the substrate are then removed by causing relative motion between the substrate and the polishing pad while providing a supply of one or more slurry compositions to the polishing surface of the polishing pad. Depending on the materials being removed, a CMP process may be primarily mechanical, wherein the material is removed by an abrasive, or a combination of chemical action between one or more components of the slurry and the one or more of the materials being removed and the mechanical action of the polisher.



**[0006]** During the planarizing process, the polishing surface of the polishing pad will typically be continuously wetted with an abrasive slurry and/or a planarizing liquid to produce the desired planarizing surface. The substrate and/or the planarizing surface of the pad are then urged into contact to establish a planarizing load or pressure and moved relative to one another to cause the planarizing surface to begin removing an upper portion of the material layer. The relative motion of the substrate and the polishing surface can be simple or complex and may include one or more lateral, rotational, revolving or orbital movements by the planarizing pad and/or the substrate in order to produce generally uniform removal of the material layer across the surface of the substrate.

**[0007]** As used herein, lateral movement is movement in a single direction, rotational movement is rotation about an axis through the center point of the rotating object, revolving movement is rotation of the revolving object about a non-centered axis and orbital movement is rotational or revolving movement combined with an oscillation. Although, as noted above, the relative motion of the substrate and the planarizing pad may incorporate different types of movement, the motion must typically be confined to a plane substantially parallel to the surface of substrate in order to achieve a planarized substrate surface.

**[0008]** The particular slurry composition, as well as the parameters under which the CMP are conducted will typically be a function of the particular characteristics of the various primary and secondary materials to be removed from the substrate surface. In particular, in a case where a polysilicon layer and a silicon oxide layer



are being polished using a silica-based slurry using silica ( $\text{SiO}_2$ ) as primary abrasive, the removal rate of the polysilicon will tend to be higher than the removal rate of the silicon oxide. These differing removal rates for different materials under substantially identical polishing conditions are typically expressed as a selectivity ratio. CMP processes are commonly arranged to take advantage of these differences in removal rate by providing a polishing stopping layer, *e.g.*, a material with a much lower removal rate, below the primary layer of material being removed to allow sufficient overpolishing to account for variations in layer thicknesses and wafer planarity. This overpolishing increases the likelihood that substantially all of the intended material layer can be removed without damaging the underlying patterns. In certain instances, however, it may not be possible or practical to utilize a polishing stopping layer, or the relative characteristics of the materials being removed can tend to result in “dishing” or “cupping” of the more easily removed material and produces a more non-planar surface than desired and may compromise subsequent processing.

[0009] For example, as illustrated in FIGS. 1A-D, the removal of the upper portion of a polysilicon layer deposited over a silicon nitride pattern can result in a substantially non-planar surface. As illustrated in FIG. 1A, a substrate 100 has an active region 102 separated by isolation regions 104. The active region 102, will also typically include one or more doped regions (not shown) to which electrical contact must be made in order for the final semiconductor device to operate properly. A pattern of gate electrodes 106 or other structures are then formed on the substrate.



The gate electrodes 106, which may have a stacked structure including polysilicon 108 and a metal silicide 110, formed by reacting a metal, such as tungsten, cobalt or nickel, or a metal alloy with a portion of the polysilicon, are protected by an insulating spacer structure 112, typically including silicon dioxide and/or silicon nitride. Between the spacer structures 112, contact portions of the surface of the semiconductor substrate will be exposed and a polysilicon layer 114 will be deposited on the structure as a means of establishing electrical contact to the substrate.

**[0010]** As illustrated in FIG. 1B, the upper portion of the polysilicon layer 114 is then removed to form polysilicon plugs 114a between the spacer structures 112. However, because polysilicon may be removed at a rate greater than the rate at which silicon oxide or silicon nitride are removed, in some instances as much as 50 to 100 times greater, there is a tendency for excessive polysilicon to be removed, forming depressions 116 between the spacer structures and produce a non-planar surface. As illustrated in FIG. 1C, once the CMP process has been completed, an interlayer dielectric layer (ILD) 118, may be deposited on the substrate. A photoresist contact pattern (not shown) will then be formed on the ILD 118 and the ILD material etched to form contact openings 120 that extend through the ILD to expose a surface of the polysilicon pads or plugs 114a.

**[0011]** However, as a result of the excessive polysilicon removal, the surface of the polysilicon plugs 114a is recessed relative to the upper surfaces of the spacer structures 112, increasing the thickness of the ILD 118 that must be removed to open



the contacts. This increased thickness can result in problems such as the underetch condition illustrated in FIG. 1E wherein the etch is not sufficient to open some or all of the contact openings, leaving regions of residual ILD 118a in the bottom of the contact openings. Similarly, as illustrated in FIG. 1F, in those instances in which the depth of the etch is sufficient to reach the polysilicon, but the contact pattern is misaligned, the contacts openings can expose the gate electrodes 106 or other conductive structures, causing shorts in region S. Both opens and shorts will reduce the process yield and/or reduce the reliability of the final semiconductor devices.

## SUMMARY OF THE INVENTION

**[0012]** The exemplary embodiments of the present invention address the noted problems of the conventional CMP processes by providing new slurry compositions that are suitable for use in processes involving the chemical mechanical polishing (CMP) of a polysilicon layer to reduce or eliminate the excessive removal of the polysilicon layer.

**[0013]** Exemplary embodiments of the present invention include methods of manufacturing semiconductor devices incorporating CMP processes that utilize slurry compositions and/or one or more slurry additives to reduce or eliminate the excessive removal of the polysilicon layer. In particular, the CMP processes according to exemplary embodiments of the invention incorporate one or more non-ionic surfactants to provide selective control over the removal rate of polysilicon relative to silicon oxide and silicon nitride. Exemplary surfactants include



copolymer alcohols of ethylene oxide (EO) and propylene oxide (PO) and may be present in the slurry compositions in an amount of up to about 5 wt%. Other slurry additives may include one or more amine or imine surfactants intended to modify the relative removal rates of silicon nitride and/or silicon oxide.

#### BRIEF DESCRIPTION OF THE DRAWINGS

**[0014]** Exemplary embodiments of the devices and methods that may be utilized to practice the present invention are addressed more fully below with reference to the attached drawings in which:

**[0015]** FIGS. 1A-F illustrate certain of the process steps in a conventional CMP method as well as certain characteristic problems associated with such processes;

**[0016]** FIGS 2A-G illustrate certain of the process steps in an exemplary CMP method according to the present invention;

**[0017]** FIGS. 3A-B are SEM images illustrating cross-sections of semiconductor devices manufactured according to the conventional method and an exemplary inventive method respectively; and

**[0018]** FIG. 4 is a graph illustrating the correlation between the amount of polymer included in the abrasive slurry composition and the polysilicon removal rate under substantially identical CMP process settings.

**[0019]** It should be noted that these Figures are intended to illustrate the general characteristics of methods and materials of exemplary embodiments of this invention, for the purpose of the description of such embodiments herein. These drawings are



not, however, to scale and may not precisely reflect the characteristics of any given embodiment, and should not be interpreted as defining or limiting the range of values or properties of embodiments within the scope of this invention.

**[0020]** In particular, the relative thicknesses and positioning of layers or regions may be reduced or exaggerated for clarity. Further, a layer is considered as being formed “on” another layer or a substrate when formed either directly on the referenced layer or the substrate or formed on other layers or patterns overlaying the referenced layer.

#### DETAILED DESCRIPTION OF EXEMPLARY EMBODIMENTS

**[0021]** Accordingly, the exemplary embodiments of the present invention comprise or incorporate a slurry composition for the chemical mechanical polishing of a polysilicon layer that includes at least a carrier liquid, abrasive particles, and a polymeric surfactant that includes both hydrophilic and hydrophobic functional groups. The polymeric surfactant will include at least one polymer alcohol including ethylene oxide (EO) and propylene oxide (PO), either as a copolymer or as a triblock polymer.

**[0022]** When used for polishing polysilicon, the hydrophobic functional groups of the polymeric surfactant attach preferentially to the exposed polysilicon surface, thereby forming a passivation layer. This passivation layer is sufficient to reduce the removal rate of the polysilicon layer relative to any exposed silicon oxide or silicon nitride surfaces and reduce or eliminate the excessive removal of polysilicon. The



slurry composition may, of course, and preferably will include additional components such as wetting agents, solvents, viscosity modifiers, pH modifiers, and buffering agents.

**[0023]** The abrasive particles may include one or more fine abrasive materials, typically one or more inorganic oxides selected from a group consisting of silica, ceria, alumina, zirconia and titania and have an average particle size of between about 5 nm and 1 $\mu$ m, preferably less than about 100 nm.

**[0024]** According to the present invention, when a CMP operation is performed on a hydrophobic material, typically polysilicon, the hydrophobic surface exposed to an exemplary slurry composition according to the present invention will accumulate or absorb a layer of the polymeric surfactant. The layer of the polymeric surfactant will, in turn, act as a passivation layer to protect the hydrophobic surface from the full effect of the polishing action of the slurry and the polishing pad. To the extent that any hydrophilic surfaces are exposed, however, they will not tend to accumulate or absorb a corresponding passivation layer of the polymeric surfactant and will, therefore, be removed at a more conventional rate by the polishing action of the slurry and polishing pad.

#### The Slurry Composition

**[0025]** Exemplary embodiments of slurry compositions according to the present invention will typically comprise a dispersion or suspension of abrasive particles in a primary carrier liquid, usually deionized water. A variety of aqueous slurry



compositions are commercially available from companies known to those in the art comprising a variety of abrasive types and sizes tailored to the removal of silicon oxide, silicon nitride, polysilicon, silicides and metals, such as tantalum and copper. The abrasive(s) may be selected from a variety of oxides including silica,  $\text{SiO}_2$ , alumina,  $\text{Al}_2\text{O}_3$ , ceria,  $\text{CeO}_2$ , and magania,  $\text{Mn}_2\text{O}_3$ . The size distribution and quantity of the abrasive particles in the slurry will have a large effect on polishing efficiency and may range from about 1 to more than 30 wt% of the slurry composition, although about 5 to 20 wt% is probably more typical.

**[0026]** The primary slurry composition, *i.e.*, the carrier liquid and the abrasive particles, may incorporate a variety of additives and/or may be selectively adjusted through the addition of one or more components as the slurry is being applied, or immediately prior to application, to the polishing surface. The additional components may include, for example, viscosity modifiers, anti-foaming agents, chelating agents and dispersal agents to obtain a slurry composition having the desired combination of properties.

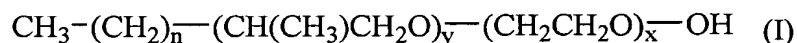
**[0027]** The pH of the slurry composition may be controlled through the introduction of appropriate acids and bases, with or without corresponding buffering agents, to produce a slurry composition within a desired pH range. Maintaining a desired slurry pH may be accomplished with bases including potassium hydroxide, KOH, ammonium hydroxide,  $\text{NH}_4\text{OH}$ , trimethylamine, TMA, triethylamine, TEA, and tetramethylammonium hydroxide, TMAH or acids including sulfuric acid,  $\text{H}_2\text{SO}_4$ , nitric acid  $\text{HNO}_3$ , hydrochloric acid, HCl, or phosphoric acid,  $\text{H}_3\text{PO}_4$ , that



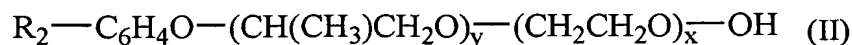
may be added in small, controlled amounts to the slurry sufficient to adjust the pH to within the desired pH range.

**[0028]** The slurry composition will further include one or more non-ionic polymeric surfactants having both a hydrophilic functional group and a hydrophobic functional group. Polar groups, those containing oxygen, nitrogen and sulfur, such as -OH, -COOH, -NH<sub>2</sub>, and -SO<sub>3</sub>H groups will tend to be hydrophilic, while aliphatic and aromatic hydrocarbon groups that do not also incorporate one or more polar groups will tend to be hydrophobic. Exemplary polymeric surfactants according to the present invention comprise a combination of ethylene oxide (EO) and propylene oxide (PO) in the form of a copolymer, *i.e.*, EO<sub>x</sub>-PO<sub>y</sub>, or a triblock copolymer, *i.e.*, EO<sub>x</sub>-PO<sub>y</sub>-EO<sub>z</sub> or PO<sub>x</sub>-EO<sub>y</sub>-PO<sub>z</sub>, in a polymer alcohol. These exemplary polymeric surfactants will bind preferentially to the hydrophobic surface of polysilicon. The polymeric surfactant(s) may be included in the slurry composition in an amount between about 0.001 to 5 wt%, and will more typically comprise between about 0.05 and 0.2 wt% based on the dry weight of the slurry composition.

**[0029]** The exemplary ethylene oxide-propylene oxide block copolymer alcohols may be selected from a group consisting of a first group of alcohols that may be represented by the formula I



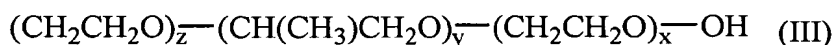
and a second group of alcohols that may be represented by the formula II



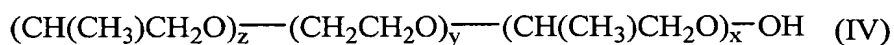


wherein  $R_2$  is  $-C_9H_{19}$  or  $-C_8H_{17}$ ;  $3 \leq n \leq 22$ ;  $1 \leq y \leq 30$ ; and  $1 \leq x \leq 30$ . Preferred alcohols are those wherein both  $x$  and  $y$  are at least 5.

**[0030]** Similarly, the exemplary ethylene oxide-propylene oxide triblock copolymer alcohols may be selected from a group consisting of a first group of alcohols that may be represented by the formula III



and a second group of alcohols that may be represented by the formula IV



wherein  $1 \leq z \leq 30$ ; and  $1 \leq y \leq 30$ ; and  $1 \leq x \leq 30$ . Preferred alcohols are those wherein both  $x$ ,  $y$  and  $z$  are at least 5.

**[0031]** The slurry composition may also include addition surfactants designed to modify the relative removal rates of silicon oxide and silicon nitride for those instances in which the polysilicon layer 114 is deposited over structures that will expose both silicon oxide and silicon nitride surfaces during the CMP process. The composition, including the pH, of the abrasive slurry need not be constant over the entire course of the CMP process but may, instead, be modified as necessary to provide an acceptable combination of removal rates, planarity and economy. The particular slurry composition(s) can be changed incrementally or significantly as the particular composition and thickness of the material(s) being removed from the substrate varies over the course of the complete CMP process.

**[0032]** For example, in the absence of the exemplary polymeric surfactants, polysilicon removal rates on the order of 4500 Å/min may be achieved with



conventional abrasive slurries. The addition of even minor amounts, *e.g.*, less than 0.02 wt%, of the exemplary polymeric surfactants, however, can reduce the polysilicon removal rate to less than 2000 Å/min but will also tend to improve planarity. By delaying the application of the exemplary polymeric surfactant(s) to the polysilicon surface until a majority of the polysilicon layer has been removed at the higher removal rates allows the process throughput to be maintained at higher levels while providing the benefit of improved planarity and decreased material costs. Similar adjustments can, of course, be made to the pH of the slurry composition as well as the concentration of other components, thereby increasing the control of the CMP process.

[0033] The production of a semiconductor device with a CMP process utilizing an exemplary polymeric surfactant according to the present invention is illustrated in FIGS. 2A-D. As illustrated in FIG. 2A, a substrate 100 has an active region 102 separated by isolation regions 104. The active region 102, will also typically include one or more doped regions (not shown) to which electrical contact must be made in order for the final semiconductor device to operate properly. A pattern of gate electrodes 106 or other structures are then formed on the substrate. The gate electrodes 106, which may have a stacked structure including polysilicon 108 and a metal silicide 110, formed by reacting a metal, such as tungsten, cobalt or nickel, or a metal alloy with a portion of the polysilicon, are protected by an insulating spacer structure 112, typically including silicon dioxide and/or silicon nitride. Between the spacer structures 112, contact portions of the surface of the semiconductor substrate



will be exposed and a polysilicon layer 114 will be deposited on the structure as a means of establishing electrical contact to the substrate.

**[0034]** As illustrated in FIG. 2B-C, the upper portion of the polysilicon layer 114 is then removed to form polysilicon plugs 114a between the spacer structures 112. However, because the polysilicon is being removed with CMP process using an exemplary slurry composition including one or more of the polymeric surfactants, a passivation layer 200 is formed on the surface of the polysilicon layer, thereby suppressing the rate at which the polysilicon will be removed. As the covering polysilicon layer 114 is removed to expose the spacer structures 112, the remaining portions of the passivation layer 200a will be substantially confined to the remaining polysilicon regions, thereby allowing substantially normal removal of the material(s) comprising the spacer structures. As a result, the depth of any depressions 116 formed between the spacer structures is reduced and a generally planar surface may be produced. As illustrated in FIG. 2E, however, the passivation layer formed on the polysilicon surfaces may be sufficient to produce a substantially planar surface exposing upper surfaces of the spacer structures and with almost no appreciable depressions corresponding to the polysilicon surfaces.

**[0035]** As illustrated in FIGS. 2F-G, once the CMP process has been completed, an interlayer dielectric layer (ILD) 118, may be deposited on the substrate. A photoresist contact pattern (not shown) will then be formed on the ILD 118 and the ILD material subsequently etched to form contact openings 120 that extend through the ILD to expose a surface of the polysilicon plugs 114a.



**[0036]** However, by suppressing the polysilicon removal through use of the polymeric surfactant, the exemplary slurry compositions are able to maintain the surface of the polysilicon plugs 114a in substantially planar orientation with the upper surfaces of the spacer structures 112. As a result, the contact openings may be etched to expose the upper surface of the polysilicon plugs 114a as illustrated in FIG. 2E and decrease the likelihood of an underetch condition as illustrated in FIG. 1E.

**[0037]** Similarly, as illustrated in FIG. 2F, by avoiding excessive removal of the polysilicon, increasing the height of the polysilicon plug 114a relative to the gate structure 106 and the spacer structure 112 provides additional overetch margin. As a result of the additional margin, it is more likely that a sufficient portion of the spacer structure 112a will remain after the contact etch process has been completed whereby a misaligned contact pattern is less likely to result in gate shorts. This additional etch margin will thereby decrease the likelihood of the situation illustrated in FIG. 1F. Because both opens and shorts will reduce the process yield and/or reduce the reliability of the final semiconductor devices, the reduction of these defects associated with CMP processes using slurry compositions according to the present invention may increase the process yield and/or reliability of the resulting devices.

**[0038]** As described above, according to the present invention, one or more exemplary polymers having both hydrophilic and hydrophobic functional groups may be incorporated into a CMP slurry used in removing an upper portion of a polysilicon layer. The configuration of the exemplary polymers produce a



passivation layer on hydrophobic surfaces, *e.g.*, polysilicon, that suppresses the removal rate of the polysilicon relative to silicon nitride and silicon oxide, thus reducing or eliminating the cupping or dishing concerns associated with excessive polysilicon and improving the planarity of the resulting surface.

#### Comparative Experimental Data

**[0039]** Semiconductor substrates corresponding to FIG. 2A were prepared and then subjected to a CMP process to remove the upper portion of the polysilicon layer and expose upper surfaces of the spacer structures. A conventional, commercially available slurry composition was obtained that included a silica abrasive having an average particle size of about 30 nm, a solids content of less than about 30 wt% and a pH modifier to maintain a pH of at least 7 during the CMP process.

**[0040]** This conventional slurry composition in both unmodified form and as modified by the addition of about 0.02 vol% of a polymeric surfactant according to the exemplary embodiments of the present invention to prepare a exemplary slurry composition. Test substrates were then polished under substantially identical CMP conditions using the conventional and exemplary slurry compositions.

**[0041]** After the polishing was completed, the polished substrates were cross-sectioned and imaged on a scanning electron microscope (SEM) to produce micrographs reproduced as FIGS. 4A and B. As reflected in the FIG. 4A, the conventional abrasive slurry composition resulted in distinct cupping of the polysilicon regions between the spacer structures. Conversely, the addition of the minor amount of polymeric surfactant according to the invention was sufficient to



suppress the excessive removal of the polysilicon layer. The magnitude of the polysilicon recesses reflected in the samples was then evaluated to generate the data reflected in TABLE 1.

Slurry Composition	Mean Depth of Recess (Å)
no exemplary surfactant	214
0.02 vol% exemplary surfactant	18

TABLE 1

[0042] As reflected in TABLE 1, therefore, even the addition of a relatively minor portion of the exemplary polymeric surfactants, *i.e.*, 0.02 vol%, produced a reduction in the depth of the polysilicon recess of more than 90%. The consumption of the exemplary polymeric surfactants in a CMP process may be reduced by limiting its use to only the final portion of the polysilicon CMP process. This practice, by not prematurely suppressing the polysilicon removal, will allow process throughput to be maintained at near conventional levels while still providing the improved planarity of the exemplary CMP methods.

[0043] It will be apparent to those skilled in the art that other changes and modifications may be made in the above-described CMP methods and slurry compositions without departing from the scope of the invention herein, and it is intended that all matter contained in the above description shall be interpreted in an illustrative and not a limiting sense.